

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

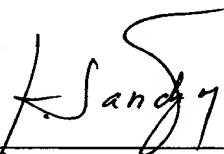
Applicants: A. M.E. Lafuente,  
et al. ) Re: Declaration  
Serial No.: 09/299,539 )  
Filed: April 26, 1999 ) GAU: 1755  
For: "Catalytic Systems for the  
Polymerization . . ." ) Examiner: J. Pasterczyk  
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DECLARATION UNDER 37 C.F.R. § 1.132

1. I, JOSE SANCHO ROYO, received a Ph.D. in CHEMISTRY from MASSACHUSETTS INSTITUTE OF TECHNOLOGY, which is located in CAMBRIDGE (MASS) USA.
2. From 1992 to the present, I have been employed as a RESEARCH SCIENTIST.
3. I am a co-inventor for the above-identified U.S. Patent Application No. 09/299,539.
4. I conducted the tests that are described in Appendix I, which is attached hereto and which is part of this Declaration.

5. I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

(Signature)



November 10<sup>th</sup> 2004

Date

JOSE SANCHEZ ROYO  
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## APPENDIX I

In order to show the advantageous use of the catalyst composition made according to the method disclosed in the instant patent application, a carefully selected set of comparative experiments was designed and performed.

Comparative metallocenes not containing the  $R^H_3SiO$  group were synthesized, with the closest molecular structures to the ones disclosed in the present application. More specifically the following metallocenes were selected:

A:  $(C_5H_4-(CH_2)_3-OSiMe_3)(C_5H_5)ZrCl_2$  [i.e., a typical metallocene of the instant patent application]

B:  $(C_5H_4-(CH_2)_3-SiMe_3)(C_5H_5)ZrCl_2$  [i.e., closest molecular structure to metallocene A without the oxygen atom and not able to produce "simultaneous interaction" with silica modified with MAO].

C:  $(C_5H_4-(CH_2)_3-CH_3)(C_5H_5)ZrCl_2$  [i.e., close molecular structure to metallocene A and typical and representative example of the metallocenes used by Welborn (similar to catalyst D in Welborn examples except in that in said catalyst both cyclopentadienyl ring are substituted with butyl groups instead of one ring only)].

### Comparative activity:

Firstly, the activity of the 3 above identified metallocenes (A, B and C) was measured in ethylene copolymerization under *homogeneous conditions*, i.e., in the absence of support, using MAO in solution.

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Copolymerization was performed under the same exact conditions for the 3 metallocenes as described in Comparative Example 20 of the present application except that 85°C was maintained instead of 70°C, 10 ml of 1-hexene was added instead of 20 ml, 5.3 ml of a solution of MAO 10% in toluene instead of 2.7 ml, 30 minutes polymerization instead of 15 minutes and the prescribed amount of metallocene as shown in Table 1. The results obtained are shown in Table 1.

**Table 1**

**Comparative activity of metallocenes A, B and C under homogeneous conditions**

Metallocene	Mmols used	Activity (gPE/mol Methxatm)	Relative activity
A	$5.7 \times 10^{-4}$	$1.25 \times 10^7$	1
B	$5.9 \times 10^{-4}$	$1.18 \times 10^7$	0.944
C	$6.9 \times 10^{-4}$	$1.03 \times 10^7$	0.824

These results show that the activity of metallocene A (instant patent application) under homogeneous conditions has similar activity than typical metallocenes also very closed in molecular structure but without the group  $OSiR_3^H$  (used for example by Welborn).

One of the objectives of the present invention is to provide supported catalysts whose activity is comparatively higher under heterogeneous condition than that obtained with other metallocenes known in the previous state of the art even if the metallocenes (present invention) used as a component to prepare the said supported catalysts show, under homogeneous conditions, similar activity.

The solution provided by the instant invention is based on the heterogeneous catalytic composition obtained by reacting a porous inorganic support with an aluminoxane and specific metallocenes containing a  $OSiR_3^H$  group such as metallocene A, for example. In order to show one of the objectives of the present invention (comparative activity of supported catalysts), 3 supported catalysts were prepared according to the method disclosed in Example 11 with the exception that the silica modified with MAO contained 14% by weight Al instead of 23% and 0.079 mmol of respective metallocene A, B or C was used instead of 0.2 mmol thus making supported catalyst with the same %Zr content (0.24 % weight).

**Supported Catalyst A:** Made as above by using metallocene A.

**Supported Catalyst B:** Made as above by using metallocene B.

**Supported Catalyst C:** Made as above by using metallocene C.

Low pressure polymerization:

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Copolymerization of ethylene and 1-hexene was performed (under the same conditions for all the 3 catalysts) as in Example 27 with the exception that 85°C was maintained instead of 70°C, 10 ml hexene was added instead of 20 ml and 30 minutes polymerization time instead of 15 minutes.

After copolymerization, the weight of polymer recovered was weighed and the productivity for the 3 catalysts calculated. The results obtained are shown in Table 2.

**Table 2**  
Comparative copolymerization activity of supported metallocenes at 4 bar

Supported catalyst	Productivity (g copolymer/g supported catalyst.hour)	Relative productivity
Supported A	398	1
Supported B	158	0.397
Supported C	174	0.437

Results of Table 2 clearly show the superior performance in activity of supported catalyst A even if the metallocene used to obtain the supported catalyst showed, under homogeneous condition (non supported, Table 1), similar activity.

In this case, comparative activity is calculated in terms of productivity per gram of supported catalyst (more useful parameter in terms of industrial practice). The content of Zr for the 3 catalysts was the same.

### High pressure copolymerization

Copolymerization of ethylene and 1-hexene was also performed (under the same conditions for all the 3 catalysts) as in Example 30 with the exception that 142 ml hexene was added instead of 49,6 ml and 30 mg of each supported catalyst was used.

After copolymerization, the weight of polymer recovered was weighed and the productivity for the 3 catalysts calculated. The results obtained are shown in Table 3.

**Table 3**  
Comparative copolymerization activity of supported metallocenes at 40 bar

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Supported catalyst	Productivity (g copolymer /g supported catalyst.hour)	Relative Productivity	Copolymer
<b>A (instant patent application)</b>	3933	1	Pol-A
<b>B</b>	2367	0.601	Pol-B
<b>C</b>	2167	0.550	Pol-C

In all cases, the productivity of the supported catalyst A (present patent application) is higher again than the productivity observed with catalysts B and C obtained following the teachings of Welborn.

It is concluded that supported catalysts obtained according to the present invention are different to the ones obtained by Welborn as explained before and its use is comparatively advantageous showing under the same conditions higher productivity.

### Polymer morphology

Formation of "fines" (small size polymer particles) creates problems in industrial operations mainly concerned with solid liquid or solid gas separations among others. So, a catalyst with reduced formation of fines would solve industrial problems and would be of high interest. Thus, other of the objectives of the present invention is to provide a supported catalyst producing polymers with reduced amount of polymer fines, lower than that known in the previous state of the art.

It is usually found that percentage of polymer fines observed under industrial operation conditions is higher than in laboratory scale but tests under later conditions are performed to *select the best* candidates even though under these conditions the comparative differences among different catalysts are smaller than in the former case.

Analysis of the polymer size particle distribution was performed for the 3 polymers products obtained: (Pol-A, Pol-B, Pol-C) obtained at 40 bar copolymerization. The relevant results obtained are shown in Table 4.

**Table 4**  
**Polymer size distribution**

Catalyst	% size < 163 microns	% size < 222 microns	% size < 300 microns
Pol-A	0.00	0.11	0.71
Pol-B	0.32	0.88	3.70
Pol-C	0.14	1.17	6.06

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These data, again, show the differential behaviour of supported catalyst A (instant patent application) in comparison with prior art catalysts. The amount of small size polymer particles using the catalyst of the present invention is lower than that obtained with prior art catalysts (Welborn).

These results are not obvious or suggested by any of the mentioned documents by the Examiner (Antberg or Welborn) and experts in the state of the art would choose preferable catalyst A if were to be used under industrial practical operation.